

**METHODS OF MAKING FOAMED MATERIALS OF BLENDED
THERMOPLASTIC POLYMERS USING CARBON DIOXIDE**

Cross-Reference to Related Applications

5 The instant application is a continuation-in-part application of Serial No. 09/399,993 filed 20 September 1999, the disclosure of which is incorporated herein by reference in its entirety.

Field of the Invention

10 The invention generally relates to methods of making foamed materials from a blend of thermoplastic polymer materials employing various blowing agents.

Background of the Invention

15 Methods for making conventional foamed materials, such as for example thermoplastic materials, have long been known. These methods have focused primarily on employing chemical and physical blowing agents that include, for example, azos, various volatile organic compounds (VOCs), and chlorofluorocarbons (CFCs). The chemical blowing agents typically
20 decompose at a critical temperature and release a gas such as nitrogen, carbon dioxide, or carbon monoxide. The physical blowing agents typically are dissolved in the polymer material and then precipitated to form a foamed structure. Conventional foaming processes are believed to be becoming increasingly undesirable. For example, the use of these organic compounds
25 has received heightened scrutiny due to potential environmental risks associated with the same. Moreover, conventional foaming processes often

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Semicrystalline polymers present various processing challenges, particularly with respect to producing microcellular foams via a continuous processing. Structural foams, along with other conventional foams, typically proceed commercially with physical blowing agents and semicrystalline polymers. Nonetheless, problems with these foams tend to stem from the small size of the cell walls, and a small defect in the cell wall is often a significant weak point in the structure leading to the observed problems. Producing various foamed semicrystalline thermoplastic polymers such as (poly)vinylidene fluoride in a continuous process has often been observed to be problematic. It has been observed that as the material exits the nozzle of a foaming system, the extrudate often becomes brittle and breaks up into fine powder. Although not wishing to be bound by theory, it is believed that the semicrystalline nature of polymer causes the extrudate to break into small particles when the blowing agent is released. This tends to be most significant in the formation of a microcellular foams, where the large number of small well-distributed cells creates a situation in which the cell walls of the foamed material are significantly thinner than those of conventional foams.

There is a need in the art to provide foamed polymers which avoid the problems stated above, particularly with respect to semicrystalline polymers.

30 Summary of the Invention

In one aspect, the invention provides a method of producing a foamed material. The method comprises contacting a mixture comprising a first thermoplastic polymer and a second thermoplastic polymer with a blowing agent. The first thermoplastic polymer has a higher percent crystallinity than

the second thermoplastic polymer. The mixture of thermoplastic polymers is then subjected to conditions sufficient to create a thermodynamic instability in the blend to foam the mixture. The mixture comprising the first and second thermoplastic polymers has a percent crystallinity lower than the first thermoplastic polymer.

In another aspect, the invention provides a method of extrusion processing a blend of thermoplastic materials. The method comprises introducing at least two thermoplastic polymers into an extruder barrel. The at least two thermoplastic polymers comprise a first thermoplastic polymer and a second thermoplastic polymer. The first thermoplastic polymer has a higher percent crystallinity than the second thermoplastic polymer. The blend of thermoplastic materials is then heated to provide a molten blend thereof. The molten blend is then contacted with a blowing agent, and the blend is subjected to conditions sufficient to create a thermodynamic instability in the blend to foam the blend. The blend has a percent crystallinity lower than the first thermoplastic polymer.

Other aspects and advantages of the invention are set forth in detail herein.

Brief Description of the Drawings

FIG. 1 illustrates an extruder to be used in accordance with the invention;

FIG. 2 illustrates an injection molding device to be used in accordance with the invention;

FIG. 3 illustrates a pultrusion device to be used in accordance with the invention;

FIG. 4 illustrates a batch reactor to be employed in accordance with the invention;

FIGS. 5A and 5B illustrate scanning electron micrographs (imaged with backscattered electrons) of uncoated (a) PMMA foam produced with 6 weight percent supercritical CO₂ and (b) PVDF foam generated with 2 weight percent supercritical CO₂;

FIG. 6 illustrates viscosity as a function of shear rate at 210°C for neat

PVDF (E) and PMMA (J), as well as several PVDF/PMMA blends differing in composition (designated in the figure legend);

FIG. 7 illustrates the dependence of viscosity on shear rate at 210°C for PVDF in the presence of 2 weight percent supercritical CO₂, as well as for three PVDF/PMMA blends (compositions identified in the figure legend) 4 weight percent supercritical CO₂. Solid lines serve as guides. Lines representing data acquired from neat PVDF and PMMA in the absence of supercritical CO₂ are included for comparison with FIG. 2;

FIGS. 8A through D illustrate backscattered electron images of PVDF/PMMA foams differing in composition (in weight percent PVDF) — (a) 20, (b) 40) and (c) 80 — generated with 6 weight percent supercritical CO₂.

Detailed Description of the Preferred Embodiments

The present invention now will be described more fully hereinafter with reference to the accompanying specification, drawings, and examples, in which preferred embodiments of the invention are shown. This invention may, however, be embodied in many different forms and should not be construed as limited to the embodiments set forth herein. Rather, these embodiments are provided so that this disclosure will be thorough and complete, and will fully convey the scope of the invention to those skilled in the art.

In one aspect, the invention relates to a method of producing a foamed material. The method comprises contacting a material with a fluid mixture comprising carbon dioxide and a surfactant, wherein the surfactant facilitates the dissolution of the carbon dioxide into the material to foam the material.

The fluid mixture is preferably homogeneous on the macroscopic scale, i.e., greater than about 1 micron. The use of the surfactant is believed to aid in lowering the interfacial tension between the carbon dioxide and the polymer.

In a preferred embodiment, a microcellular material is formed. For the purposes of the invention, the term "microcellular material" refers to material having an average cell size ranging from above 0 to about 500 microns, more preferably from about 1 to about 100 microns, and most preferably from about 0.1 to about 50 microns.

For the purposes of the invention, carbon dioxide is employed as a fluid in a liquid, gaseous, or supercritical phase. If liquid CO₂ is used, the temperature employed during the process is preferably below 31°C. If gaseous CO₂ is used, it is preferred that the phase be employed at high
5 pressure. As used herein, the term "high pressure" generally refers to CO₂ having a pressure from about 50 to about 500 bar. In one embodiment, the CO₂ is utilized in a "supercritical" phase. As used herein, "supercritical" means that a fluid medium is above its critical temperature and pressure, i.e., about 31°C and about 71 bar for CO₂. The thermodynamic properties of CO₂
10 are reported in Hyatt, *J. Org. Chem.* **49**: 5097-5101 (1984); therein, it is stated that the critical temperature of CO₂ is about 31°C; thus the method of the present invention may be carried out at a temperature above 31°C. For the purposes of the invention, it is preferred to employ CO₂ at a pressure ranging from at a lower end of about 20 or about 50 bar to an upper end of about 200
15 bar or about 1000 bar. In certain embodiments (e.g., extrusion), CO₂ may be introduced into a system at about 270 bar to about 340 bar. The pressure may then drop to about 100 bar to about 170 bar subsequent to introduction of the CO₂.

In some embodiments, it may be advantageous to carry out the
20 invention at lower temperatures that may be subambient such as, for example, a range from about 15°C to about 25°C, and more preferably about 15°C.

Materials that may be foamed as a result of the method of the invention are numerous and known in the art. For the purposes of the invention, the
25 term "foamed material" refers to a material having a plurality of distinct void spaces formed therein. As an example, the material may be selected from the group consisting of a polymer, a metal, and food products such as, but not limited to, doughs employed in baking and pastas. Preferred metals include aluminum and alloys thereof. The material to be foamed may comprise a
30 polymeric precursor such as, for example, a thermoset precursor. Exemplary thermoset precursors include, but are not limited to, epoxy resins, resole, novolacs, polyurethanes, and polyurea, which is often useful for coating materials such as powder coatings. The term "polymer" is to be broadly construed to include, but not be limited to, a homopolymer, copolymer,

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terpolymer, and the like. Crystalline, semicrystalline, and amorphous polymeric materials can all be foamed as a result of the method of the invention. Polymers that may be foamed include, for example, thermoplastic and thermoset polymers. A polymer that is foamed is preferably a

5 thermoplastic polymer. Exemplary thermoplastic polymers include, but are not limited to, polyvinyl chloride, polyolefins (e.g., high and low density polyethylene, high and low density polypropylene, and the like), nylons, fluoropolymers such as, but not limited to, those described in U.S. Patent No. 5,674,957 to DeSimone et al., the disclosure of which is incorporated herein

10 by reference in its entirety (e.g., polyvinylidene fluoride, polyvinyl fluoride, polytetrafluoroethylene, polychlorotrifluoroethylene, polyhexafluoroisobutylene, and others), polyurethane, polystyrene, polycarbonate, polyethylene terephthalate, polymethyl methacrylate, and cellulosic and acrylic resins. Blends and mixtures of the above may also be used. In

15 general, the foamed materials may be useful in a number of forms such as, but not limited to, sheet form, tubes, cylinders, fibers, and non-wovens.

The surfactants which are employed by the processes of the invention are known to those skilled in the art. Preferably, the surfactants are non-ionic surfactants. Examples of suitable surfactants are set forth in U.S. Patent Nos.

20 5,783,082; 5,589,105; 5,639,836; and 5,451,633 to DeSimone et al.; 5,676,705; and 5,683,977 to Jureller et al., the disclosures of which are incorporated herein by reference in their entirety. In general, the surfactant may encompass any macromolecule that serves to emulsify, that may be polymeric or non-polymeric.

25 Preferably, the surfactant has a segment that has an affinity for the material it comes in contact with, or, stated differently, a "CO₂-phobic segment". In embodiments wherein thermoplastic polymers are foamed, the "CO₂-phobic" segment has an affinity for the polymer material. Exemplary CO₂-phobic segments may comprise common lipophilic, oleophilic, and

30 aromatic polymers, as well as oligomers formed from monomers such as ethylene, α -olefins, styrenics, acrylates, methacrylates, ethylene oxides, isobutylene, vinyl alcohols, acrylic acid, methacrylic acid, and vinyl pyrrolidone. The CO₂-phobic segment may also comprise molecular units containing various functional groups such as amides; esters; sulfones;

may also be employed. Exemplary siloxane-containing segments include alkyl, fluoroalkyl, and chloroalkyl siloxanes. More specifically, dimethyl siloxanes and polydimethylsiloxane materials are useful. Mixtures of any of the above may be used. In certain embodiments, the "CO₂-philic" segment
5 may be covalently linked to the "CO₂-phobic" segment.

Surfactants that are suitable for the invention may be in the form of, for example, homo, random, block (e.g., di-block, tri-block, or multi-block), blocky (those from step growth polymerization), and star homopolymers, copolymers, and co-oligomers. Exemplary homopolymers include, but are not limited to,
10 poly(1,1'-dihydroperfluorooctyl acrylate) ("PFOA"), poly(1,1'-dihydroperfluorooctyl methacrylate) ("PFOMA"), poly(2-(N-ethylperfluorooctane-sulfonamido) ethyl methacrylate) ("PEtFOSEMA"), and poly(2-(N-ethylperfluorooctane sulfonamido) ethyl acrylate) ("PEtFOSEA"). Exemplary block copolymers include, but are not limited to, polystyrene-b-poly(1,1-
15 dihydroperfluorooctyl acrylate), polymethyl methacrylate-b-poly(1,1-dihydroperfluorooctyl methacrylate), poly(2-(dimethylamino)ethyl methacrylate)-b-poly(1,1-dihydroperfluorooctyl methacrylate), and a diblock copolymer of poly(2-hydroxyethyl methacrylate) and poly(1,1-
20 dihydroperfluorooctyl acrylate) and polystyrene, along with poly(1,1-dihydroperfluorooctyl methacrylate) and poly(2-hydroxyethyl methacrylate) can also be used. Graft copolymers may be also be used and include, for example, poly(styrene-g-dimethylsiloxane), poly(methyl acrylate-g-
1,1'-dihydroperfluorooctyl methacrylate), and poly(1,1'-dihydroperfluorooctyl
25 acrylate-g-styrene). Random copolymers may be employed and examples of such include, but are not limited to, copolymers or terpolymers of tetrafluoroethylene, vinylidene fluoride, hexafluoropropylene, chlorotrifluoroethylene, and ethylene. Other examples can be found in I. Piirma, *Polymeric Surfactants* (Marcel Dekker 1992); and G. Odian,
30 *Principals of Polymerization* (John Wiley and Sons, Inc. 1991). It should be emphasized that non-polymeric molecules may be used such as perfluoro octanoic acid, surfynols, perfluoro(2-propoxy propanoic) acid, fluorinated alcohols and diols, along with various fluorinated acids, ethoxylates, amides, glycosides, alkanolamides, quaternary ammonium salts, amine oxides, and

amines. Commercially preferred surfactants include, for example those in the Zonyl® series sold by E.I. Du Pont de Nemours of Wilmington, Delaware and those in the Fluorad® series sold by Minnesota Mining and Manufacturing of St. Paul, Minnesota. Mixtures of any of the above may be used. Various components which are suitable for the process of the invention are encompassed by the class of materials described in E. Kissa, *Fluorinated Surfactants: Synthesis, Properties, and Applications* (Marcel Dekker 1994). For the purposes of the invention, two or more surfactants may be employed in the invention. Edible surfactants may also be used.

Depending on the number of different type of polymers or polymer resins present in a blend thermoplastic material, the surfactant can comprise multiple blocks or segments which may be equal to the number of polymers or resins present in the blend. As an example, if two polymers or polymer resins are present as a blend, the surfactant may comprise two blocks or segments wherein each has an affinity for each polymer or polymer resin. If three polymers or polymer resins are employed, the surfactant may comprise three blocks or segments, and so on. In these embodiments, the surfactant may also include a "CO₂-philic" segment.

Although a number of examples of surfactants listed herein are in the form of block, random, or graft copolymers, it should be appreciated that other copolymers that are not block, random, or graft may be used.

The amount of surfactant that is used in the fluid mixture may be selected from various values. Preferably, the fluid mixture comprises from about 0.0001 to about 10 percent by weight of the surfactant, and more preferably from about 0.01 to about 2 percent by weight. It should be appreciated that this amount depends on several factors including the stability of the surfactant and desired end product.

Applicants have found that using a surfactant affords many unexpected advantages. By virtue of being present in the fluid mixture, the surfactant is able to reduce the surface tension between the material (e.g., thermoplastic polymer or polymer blend) and carbon dioxide. Thus, the surfactant is able to enhance the dissolution, entrainment, or solubility of the carbon dioxide in the material. Moreover, the reduction in surface tension is also able to modify the final foam structure of the solid foamed material. Also, employing a surfactant

aids in controlling the porosity of the foamed material. The surfactant is also capable of modifying the nucleation and/or growth rates of the voids in the materials. In the event that two or more materials are employed (e.g., thermoplastic resins), the surfactant can also be used to improve the blend compatibility between these materials in the fluid mixture, both during and after the foaming process takes place. The surfactant is also able to facilitate a reduction in viscosity of the material in the fluid mixture prior to foaming. In addition, the surfactant may act as a control parameter of the final foamed material.

10 The fluid mixture may also comprise components in addition to those described above. Exemplary components include, but are not limited to, polymer modifier, water, toughening agents, colorants, dyes, biological agents, rheology modifiers, plasticizing agents, flame retardants, antibacterial agents, flame retardants, and viscosity reduction modifiers. Co-solvents and
15 co-surfactants may also be employed.

Exemplary co-solvents that could be used include, but are not limited to, alcohols (e.g., methanol, ethanol, and isopropanol); fluorinated and other halogenated solvents (e.g., chlorotrifluoromethane, trichlorofluoromethane, perfluoropropane, chlorodifluoromethane, and sulfur hexafluoride); amines
20 (e.g., N-methyl pyrrolidone); amides (e.g., dimethyl acetamide); aromatic solvents (e.g., benzene, toluene, and xylenes); esters (e.g., ethyl acetate, dibasic esters, and lactate esters); ethers (e.g., diethyl ether, tetrahydrofuran, and glycol ethers); aliphatic hydrocarbons (e.g., methane, ethane, propane, ammonium butane, n-pentane, and hexanes); oxides (e.g., nitrous oxide);
25 olefins (e.g., ethylene and propylene); natural hydrocarbons (e.g., isoprenes, terpenes, and d-limonene); ketones (e.g., acetone and methyl ethyl ketone); organosilicones; alkyl pyrrolidones (e.g., N-methyl pyrrolidone); paraffins (e.g., isoparaffin); petroleum-based solvents and solvent mixtures; and any other compatible solvent or mixture that is available and suitable. Mixtures of the
30 above co-solvents may be used.

Exemplary co-surfactants that may possibly be used include, but are not limited to, longer chain alcohols (i.e., greater than C₈) such as octanol, decanol, dodecanol, cetyl, laurel, and the like; and species containing two or more alcohol groups or other hydrogen bonding functionalities; amides;

amines; and other like components. Suitable other types of materials that are useful as co-surfactants are well known by those skilled in the art, and may be employed in the process of the present invention. Mixtures of the above may be used. When employed, the co-surfactant may be in the form of a

5 compatibilizer. With respect to the present invention, a compatibilizer aids in helping a blend of thermoplastic polymers to be foamed retain its stability particularly after the carbon dioxide has been vented to the atmosphere. The compatibilizer can be utilized in a number of ways. In one embodiment, the compatibilizer may be pre-made and mixed in with the blend of polymers. In
10 another embodiment, the compatibilizer can be formed during any of the methods of the invention. In this instance, reactive groups are present on the polymer blend to be foamed, with the reactive groups subsequently reacting to provide compatibilization.

The invention can be employed in conjunction with a number of
15 processes including, but not limited to, extrusion, pultrusion, injection molding, and in the manufacture of non-wovens and multilayer foamed materials. The invention may be carried out as a batch, semicontinuous, or continuous process.

In another aspect, the invention provides a method of producing a
20 foamed material. The method comprises contacting a mixture comprising a first thermoplastic polymer and a second thermoplastic polymer with a blowing agent. The first thermoplastic polymer has a higher percent crystallinity than the second thermoplastic polymer. The mixture is then subjected to conditions sufficient to create a thermodynamic instability in the mixture to
25 foam the mixture. The mixture comprising the first and second thermoplastic polymers has a percent crystallinity lower than the first thermoplastic polymer. Preferably, a microcellular foam is formed, with the term "microcellular" being preferably defined herein.

The term "mixture" when used in the context describing the first and
30 second thermoplastic polymers is to be broadly construed and include various combinations of these polymers, e.g., the polymers may be compatible or non-compatible. For the purposes of the invention, the term "compatible" refers to the polymer mixture being homogeneous (or miscible) either intrinsically (i.e., without the presence of a compatibilizing aid) or by

inducement through employment of an appropriate compatibilizing aid. Heterogeneous or immiscible mixtures are also within the scope of the invention. Partially miscible mixtures are also appropriate. For the purposes of the invention, a "partially miscible" mixture refers to a system displaying

5 miscibility over a portion of the blend composition.

In certain embodiments, when the mixture of thermoplastic polymers is heated above the melting point of both polymers, the mixture may be transformed into a blend. In this case, the polymers are in the molten state. Mechanical agitation may also be employed to facilitate blend formation.

10 Non-molten blends are also contemplated for the purposes of the invention.

The term "blowing agent" refers to those materials which are useful in making foamed structures. Examples of blowing agents include, but are not limited to, inorganic agents, organic blowing agents, and chemical blowing agents. Examples of inorganic blowing agents include, but are not limited to,

15 carbon dioxide, nitrogen, argon, water, air nitrogen, and helium. Examples of organic blowing agents include, without limitation, aliphatic hydrocarbons having 1-9 carbon atoms, aliphatic alcohols having 1-3 carbon atoms, and fully and partially halogenated aliphatic hydrocarbons having 1-4 carbon atoms. Exemplary aliphatic hydrocarbons that may be used include, without

20 limitation, methane, ethane, propane, n-butane, isobutane, n-pentane, isopentane, neopentane, and the like. Exemplary aliphatic alcohols include, without limitation, methanol, ethanol, n-propanol, and isopropanol. Fully and partially halogenated aliphatic hydrocarbons can be used and include, without limitation, fluorocarbons, chlorocarbons, and chlorofluorocarbons. Examples

25 of fluorocarbons include methyl fluoride, perfluoromethane, ethyl fluoride, 1,1-difluoroethane (HFC-152a), 1,1,1-trifluoroethane (HFC-143a), 1,1,1,2-tetrafluoroethane (HFC-134a), pentafluoroethane, difluoromethane, perfluoroethane, 2,2-difluoropropane, 1,1,1-trifluoropropane, perfluoropropane, dichloropropane, difluoropropane, perfluorobutane, perfluodichloropropane, difluoropropane, perfluorobutane,

30 perfluorocyclobutane. Partially halogenated chlorocarbons and chlorofluorocarbons for use in this invention include methyl chloride, methylene chloride, ethyl chloride, 1,1,1-trichloroethane, 1,1-dichloro-1-fluoroethane (HFC-141b), 1-chloro-1,1-difluoroethane (HCFC-142),

chlorodifluoromethane (HCFC-22), 1,1-dichloro-2,2,2-trifluoroethane (HCFC-123) and 1-chloro-1,2,2,2-tetrafluoroethane (HCFC-124). Fully halogenated chlorofluorocarbons include trichloromonofluoromethane (CFC-11), dichlorodifluoromethane (CFC-12), trichlorotrifluoroethane (CFC-113), 1,1,1-trifluoroethane, pentafluoroethane, dichlorotetrafluoroethane (CFC-114), chloroheptafluoropropane, and dichlorohexafluoropropane.

Examples of chemical blowing agents that can be used include, without limitation, azodicarbonamide, azodiisobutyronitrile, benzenesulfonylhydrazide, 4,4-oxybenzene sulfonylsemicarbazide, p-toluene sulfonyl semicarbazide, barium azodicarboxylate, N,N'-dimethyl-N,N'-dinitrosoterephthalamide, and trihydrazino triazine.

The blowing agents may be used in various states (e.g., gaseous, liquid, or supercritical). Carbon dioxide is a preferred blowing agent for the purposes of the invention. Preferably, from about 2 to about 20 percent of blowing agent is used based on the weight of the mixture of thermoplastic polymers, and more preferably from about 5 to about 10 percent by weight of blowing agent is used.

The blowing agent may comprise gaseous, liquid and/or supercritical carbon dioxide as described herein above. The blowing agent may also include any of the additives (e.g., cosolvents, surfactants, modifiers, and the like) set forth herein.

The term "polymer" is to be broadly construed and encompasses, without limitation, homopolymers, copolymers, terpolymers, and the like.

The thermoplastic polymers employed in the blend can be amorphous and/or semicrystalline. The term "amorphous" refers to the polymer having no crystallinity, and the term "semicrystalline" refers to the polymer having crystallinity. Various embodiments of amorphous and semicrystalline polymers may be employed. For example, at least one of the first and second thermoplastic polymers may be amorphous and/or at least one of the first and second thermoplastic polymers may be semicrystalline. In one embodiment, the first thermoplastic polymer is semicrystalline and the second thermoplastic polymer is amorphous. In another embodiment, the first thermoplastic

polymer is semicrystalline and the second thermoplastic polymer is semicrystalline.

For the purposes of the invention, the resulting mixture of thermoplastic polymers that is foamed may be semicrystalline or amorphous provided it has
5 a lower percent crystallinity than the first thermoplastic polymer. It is preferred that the mixture of thermoplastic polymers is amorphous.

A number of different polymers may be used for the first and second thermoplastic polymers, with the first and second thermoplastic polymers being independently selected. Such polymers include, but are not limited to,
10 poly(vinylidene fluoride) (PVDF), syndiotactic polystyrene (sPS), poly(tetrafluoroethylene) (PTFE), poly(vinyl chloride) (PVC), Nylon (6,6), poly(vinylmethyl ether), polypropylene (PP), polyethylene (PE), high density polyethylene (HDPE), poly(vinyl fluoride) (PVF), poly(vinylidene chloride) (PVDC), poly(vinyl alcohol) (PVOH), poly(vinyl acetate) (PVAc),
15 polycarbonate (PC), polystyrene (PS), poly(methylmethacrylate) (PMMA), poly(isobutylene), poly(dimethylsiloxane) (PDMS), poly(ethylene oxide) (PEO), poly(ethyl acetate), poly(ethylene terephthalate) (PET), poly(ethylene naphthalate), poly(ϵ -caprolactone), poly(ether imide), poly(phenylene oxide), and poly(1,4-butylen adipate). Chemical derivatives of the above
20 thermoplastic polymers may be employed, along with mixtures of any of the above.

Examples of classes of first thermoplastic polymers that can be employed include, but are not limited to, polyesters, polycarbonates, polyamides, polyimides, polyolefins, polyurethanes, and mixtures thereof.
25 Specific thermoplastic polymers include, but are not limited to, PVDF, sPS, PTFE, PVC, Nylon (6,6), polyvinylmethylether, PP, PE, HDPE, PVF, PVDC, PVOH, PVAc, PC, poly(ethyl acetate), PET, poly(ethylene naphthalate), poly(ϵ -caprolactone), poly(ether imide), chemical derivatives thereof, and mixtures thereof. Examples of classes of second thermoplastic polymers that
30 may be used include, but are not limited to, polyolefins, polycarbonates, sytrenics, methacrylates, polyurethanes, polysulfones, polyimides, and mixtures thereof.

Specific examples of second thermoplastic polymers include, but are not limited to, PS, PMMA, polyisobutylene, PVA, PDMS, PEO, poly(phenylene oxide), PC, chemical derivatives thereof, and mixtures thereof.

A preferred first and second thermoplastic polymer mixture is PVDF being employed as the first thermoplastic polymer and PMMA being employed as the second thermoplastic polymer.

Various amounts of first and second thermoplastic polymers may be employed in the mixture. Preferably, the mixture comprises from about 90 to about 50 percent of the first thermoplastic polymer based on the weight of the mixture, and more preferably from about 80 to about 60 percent by weight. Preferably, the mixture comprises from about 10 to about 50 percent of the second thermoplastic polymer based on the weight of the mixture, and more preferably from about 20 to about 40 percent by weight.

The term "thermodynamic instability" refers to effecting a change in the temperature and/or pressure of the blend of thermoplastic polymers such that the mixture (e.g., blend) forms a foamed material. The step of subjecting the mixture to conditions sufficient to create a thermodynamic instability may be carried out in any number of ways. For example, in one embodiment, the step comprises separating the mixture from the blowing agent to foam the mixture. Preferably, the step of separating the mixture comprises venting the blowing agent, although other techniques may be employed.

It is particularly preferred that the method of employing the first and second thermoplastic polymers be carried out as a continuous process, although other types of processes may be used as known by one skilled in the art.

The method of forming the mixture of thermoplastic polymers may be carried out in a number of processing applications. As an example, in another aspect, the invention relates to a method of extrusion processing a blend of thermoplastic materials. The method comprises introducing at least two thermoplastic polymers into an extruder barrel, the at least two thermoplastic polymers comprising a first thermoplastic polymer and a second thermoplastic polymer. The first thermoplastic polymer has a higher crystallinity than the second thermoplastic polymer. The mixture of thermoplastic materials is then heated to provide a molten blend thereof. The molten blend of thermoplastic

[illegible]

materials is then contacted with a blowing agent. The blend is then subjected to conditions sufficient to create a thermodynamic instability in the blend to foam the blend. The foamed blend has a percent crystallinity lower than the first thermoplastic polymer. The above method is preferably carried out as a continuous process.

The above method may be carried out in a variety of embodiments. As an example, in one embodiment, the step of contacting the molten blend of thermoplastic materials may occur in a mixing section of the extruder. The subjecting step may be carried out, without limitation, to those embodiments described herein.

In another aspect, the invention relates to a composition of matter. The composition of matter comprises a mixture comprising a first thermoplastic polymer and a second thermoplastic polymer and a blowing agent. The first thermoplastic polymer has a higher crystallinity than the second thermoplastic polymer and the mixture comprising the first and second thermoplastic polymers has a crystallinity lower than the first thermoplastic polymer.

The terms "blowing agent", "first thermoplastic polymer", "second thermoplastic polymer", and "thermodynamic instability" as referred to in the above composition of matter are defined herein.

The aspects of the invention relating to methods of foaming mixtures of thermoplastic polymers in which the crystallinity of the mixtures are reduced, and compositions thereof are advantageous. For example, methods of foaming blends of thermoplastic polymers wherein the crystallinity is reduced may be carried out with a static mixing device or with no mixing during the step of subjecting the blend to conditions sufficient to create a thermodynamic instability in the blend foam the blend. Thus, the use of dynamic mixing during this step as alluded to in U.S. Patent No. 5,889,069 to Suh et al. may be avoided. Moreover, in certain embodiments, the addition of a percentage of amorphous thermoplastic polymer (preferably from about 20 to about 40 percent based on the weight of the mixture), allows for an increase of the solubility of the carbon dioxide in the mixture. Preferably, the solubility of the carbon dioxide in the mixture increases to at least 6 percent by weight. Although not intending to be bound by theory, it is believed that the greater carbon dioxide solubility increases the number density of bubble nucleation

sites, and, consequently, decreases in cell diameter and bulk density in a foamed polymer blend. Again not intending to be bound by theory, the increase in carbon dioxide solubility is believed to enhance the degree of plasticization and reduce the viscosity of the molten blend.

5

Extrusion

An embodiment of the invention describing an extrusion process will now be described in detail with respect **FIG. 1**. The extruder **10** is a conventional extruder which has a barrel **20** with a screw **30** positioned
10 therein. Solid material, typically in the form of pellets, is introduced into the extruder via hopper assembly **40**. The extrusion barrel is heated to conditions such that the material becomes molten. In the event that thermoplastic material is used, the material often becomes plasticized. The material is then mixed in the barrel by virtue of the motion screw **30** which
15 transports the molten material along the longitudinal axis **I** of the barrel. Carbon dioxide is subsequently introduced to the barrel **20** of extruder **10** through inlet **50**. The carbon dioxide may be in various states (e.g., gaseous, liquid, or supercritical). It may be desirable to preheat the carbon dioxide before insertion to prevent too sudden an increase in pressure in the barrel **20**
20 at a higher temperature of the barrel **20**. The surfactant and other optional additives are typically introduced into the extruder in combination with the carbon dioxide although other techniques of introducing the surfactant and other optional additives may be employed.

The carbon dioxide and the molten material are then mixed in a section
25 **60** of the barrel **20** downstream of inlet **50**. In section **60**, the carbon dioxide penetrates or diffuses into the material. This mixing continues as the carbon dioxide and material passed through adapter **70** having a static mixer present therein. The carbon dioxide and molten material is typically a single phase at this stage. Although not being bound by any theory, it is believed that
30 convective diffusion helps to completely dissolve the carbon dioxide in the material. The mixture of material and carbon dioxide is then transported to heat exchanger **80**. In this embodiment, heat exchanger **80** employs circulating fluid denoted by the arrows **x** and **y**, although other variations of this embodiment may be encompassed by the invention. In an embodiment

wherein the material is a thermoplastic polymer, the temperature of the carbon dioxide/polymer mixture is cooled to near the polymer glass transition temperature (T_g) at which point the viscosity of the polymer is observed to increase dramatically.

5 The carbon dioxide/material mixture then passes through nozzle 90 and nucleation die 100. During this time, the material typically experiences a rapid pressure drop and hence a sudden decrease in the solubility of the carbon dioxide in the material. Accordingly, a large number of bubbles usually nucleate almost instantaneously in the matrix of the material, and as a
10 result a foamed material is formed upon exiting die 100. The foamed material may be further processed in an article of manufacture as desired by the end user.

Injection Molding

FIG. 2 illustrates an injection molding device 200 that may be used in accordance with the method of the invention. Solid material, preferably thermoplastic material, is fed into the chamber 220 of the injection molding device 200 via hopper 210. The solid material is typically present in the form of pellets. The chamber is heated by a suitable technique such that the solid material is melted. Hydraulic cylinder 230 applies pressure to screw 240 such that the molten material becomes sufficiently mixed.

Carbon dioxide is then introduced into chamber **220** through line **250** along with a surfactant and other suitable additive if desirable. The carbon dioxide is then mixed with the molten polymer along the longitudinal axis **1'** of chamber **220** by virtue of the rotation of screw **240**. If carbon dioxide is employed at high pressure (e.g., in a liquid or supercritical phase), the chamber should be modified to withstand such conditions. For example, employing a nozzle **260** at the exit of the chamber **220** can be used to create a sufficient level of back pressure. Other design modifications may be made as known by the skilled artisan.

The polymer/carbon dioxide mixture then is injected through nozzle **260** into molding cavity **270** that is shaped in the form of a desired article of manufacture. As known in the art, toward the end of the injection cycle, the pressure in the molding cavity tends to rise rapidly and the material cools and

solidifies such that the material foams. At the conclusion of the molding cycle, the molding cavity is separated from the device wherein the carbon dioxide is separated (e.g., vented) from the solid foamed article. For example, the carbon dioxide may be vented using port **280**. The resulting article can then
5 be further processed or sold commercially according to the intentions of the manufacturer.

Pultrusion

FIG. 3 illustrates a pultrusion device **300** that may be used in
10 accordance with the invention. Support material, which is typically reinforcing fiber **320** is contained in a plurality of spools **310a-d**, although other structures may be employed. Examples of materials employed as reinforcing fiber include, but are not limited to, glass, carbon, metal, aromatic polyamides, polybenzimidazoles, aromatic polyimides, and nylon. Blends and
15 combinations thereof may also be used.

From the spools **310a-d**, the reinforcing fiber **320** is guided via a pair or guides **330a** and **330b** to bath **340** containing molten material, typically thermosetting or thermoplastic material. The bath may be heated by using a technique that is suitable in the art to maintain the material in a molten state.
20 A mixture of carbon dioxide, surfactant, and at least one optional additive is injected from line **370** into the bath **340**, and the components are sufficiently mixed with the material using an appropriate stirring device or method such that the carbon dioxide dissolves into the material. In the bath, the material also impregnates the reinforcing fiber. Pullers **360a** and **360b** are employed
25 to transport the fiber through the bath. In the event that carbon dioxide is employed at high pressure (e.g., in a liquid or supercritical phase), the bath should be modified to withstand such pressure conditions. As an example, a nozzle **350** at the exit of bath **340** can be used to create a sufficient level of back pressure. Other design modifications may be made as known by one
30 skilled in the art.

Upon exit from bath **340**, the impregnated reinforced fiber **320** experiences a decrease in pressure, and accordingly the material present in the fiber foams. The fiber **320** may then be used to form various structures;

for example, the fiber may be bundled into a core structure that can be used in any number of suitable applications.

Batch

5 **FIG. 4** illustrates a batch reactor **400** that may be used in foaming a material. In this embodiment, the reactor **400** includes a chamber **410** that houses material to be foamed, carbon dioxide, surfactant, along with other possible additives. The material is typically inserted into the chamber **410** through door **420**. The batch reactor also includes thermocouple **430**,
10 pressure transducer **440**, and rupture disk **450**. Optionally, a mixer or agitator (not pictured) may be employed during the process. A conventional heater is also employed in conjunction with the batch reactor **400**.

As alluded to, the material is first placed into chamber **410** and the door is closed. The material is then heated such that it is subsequently present in
15 a molten state. As an alternative, the material may be introduced into the reactor already melted. Carbon dioxide is then introduced into the chamber **410** via inlet **460** to a pressure that may be set by the end user. The pressure is usually set such that the carbon dioxide dissolves into the material. Surfactant is also present in the system, and can be introduced into the
20 reactor through a number of different ways. For example, the surfactant may be introduced along with the material, may be introduced with the carbon dioxide, or may be introduced via a separate line in fluid communication with the chamber **410**.

The material is typically pressurized with carbon dioxide for a length of
25 time suitable to allow for a level of dissolution of the carbon dioxide into the material to allow for certain end properties to be attained in the resulting foam material. After the time period, the carbon dioxide is vented through outlet **470**. After depressurization, the foamed material is collected and prepared for end use through suitable downstream processes known to the skilled artisan.

30 In another aspect, the invention relates to a composition of matter. The composition of matter comprises a thermoplastic material; and a fluid mixture comprising carbon dioxide, and a surfactant, wherein the fluid mixture is intimately mixed with the thermoplastic material. The surfactant facilitates penetration of the carbon dioxide into the thermoplastic material to foam the

thermoplastic material. The composition of matter is present as a single (e.g., homogeneous) phase. Examples of the above components employed in the composition of matter are provided herein.

5 The invention will now be described in greater detail with respect to the examples. It should be understood that the examples are for the purposes of illustration, and in no way limit the invention that is described by the claims.

Example 1

10 A sample of polystyrene is inserted in a batch reactor and the reactor is heated to 200°C. A 0.5 weight percent sample of surfactant (polystyrene-poly(FOMA)) is mixed therein. The cell is cooled to 100°C. Carbon dioxide is injected into the reactor at 3000 psi, and the cell is allowed to equilibrate. The cell is vented rapidly, and foamed material produced as a result of the process is removed.

Example 2

The procedure according to Example 1 is carried out except that carbon dioxide and surfactant are injected to the reactor simultaneously.

Example 3

20 The procedure according to Example 1 is carried out except that the cell is equilibrated at 200°C, then cooled, and then vented.

Example 4

25 The procedure according to Example 1 is carried out except that polyvinylidene fluoride is foamed.

Example 5

30 The procedure according to Example 1 is carried out except that aluminum is foamed.

Example 6

The procedure according to Example 1 is carried out except that polycarbonate is foamed.

Example 7

The procedure according to Example 1 is carried out except that polyethylene terephthalate is foamed.

5

Example 8

The procedure according to Example 1 is carried out except that polymethyl methacrylate is foamed.

10

Example 9

The procedure according to Example 1 is carried out except that high density polyethylene is foamed.

Example 10

15

The procedure according to Example 1 is carried out except that low density polyethylene is foamed.

Example 11

20 The procedure according to Claim 1 is carried out except that a thermoset precursor is foamed.

Examples 12-22

25 Examples 1-11 are repeated except that a block copolymer of polystyrene and PTFE is employed as a surfactant.

Examples 23-33

Examples 1-11 are repeated except that a block copolymer of polystyrene and PDMS is employed as a surfactant.

30

Example 34

An extruder is loaded with polystyrene and a block copolymer of polystyrene and poly(FOMA) as surfactant. The polymers are melted at 200°C. Carbon dioxide is injected at 25°C, 4500 psi such that the polymer/surfactant/carbon dioxide mixture forms a homogeneous phase

having 5 percent by weight of surfactant. The extruded mixture is cooled to 150°C, and exits via a nozzle.

Example 35

5 The procedure according to Example 34 is carried out except that polyvinylidene fluoride is foamed.

Example 36

10 The procedure according to Example 34 is carried out except that polycarbonate is foamed.

Example 37

15 The procedure according to Example 34 is carried out except that polyethylene terephthalate is foamed.

Example 38

 The procedure according to Example 34 is carried out except that polymethyl methacrylate is foamed.

Example 39

20 The procedure according to Example 34 is carried out except that aluminum is foamed.

Example 40

25 The procedure according to Example 34 is carried out except that high density polyethylene is foamed.

Example 41

30 The procedure according to Example 34 is carried out except that low density polyethylene is foamed.

Example 42

 The procedure according to Example 34 is carried out except that a thermoset precursor is foamed.

Examples 43-51

Examples 34-42 are repeated except that a block copolymer of polystyrene and PTFE is employed as a surfactant.

5

Examples 52-60

Examples 34-42 are repeated except that a block copolymer of polystyrene and PDMS is employed as a surfactant.

Examples 61-70

10 Examples 61 through 70 generally describe the foaming of semicrystalline and amorphous polymers in accordance with the invention. The polymers may be obtained from known sources. PVDF (Kynar® 740) and PMMA (Plexiglas® PM-100) employed in this study are provided by Elf Atochem N.A. of King of Prussia, Pennsylvania in pellet form and are used as
15 received. Carbon dioxide (greater than 99.8% pure) is obtained from National Specialty Gases of Durham, North Carolina. Blends of PVDF and PMMA were prepared by mixing predetermined masses of PVDF and PMMA to yield a desired composition. Pellets from the homopolymers are mixed at 200°C in a single-screw extruder manufactured by Wayne Machine and Die Co. of
20 Totowa, New Jersey. The mixed molten blend is then cooled to 150°C and a thermodynamic instability is induced to obtain the foamed sample. Foamed samples are dried under vacuum for 24 hours at 50°C, fractured in liquid nitrogen, and examined in a Hitachi S3200N variable-pressure scanning electron microscope sold by Hitachi Instruments, Inc. of San Jose, California.
25 Backscattered electron images of uncoated foams are acquired at an accelerating voltage of 21kV and a chamber pressure of 50 Pa. The viscosities of the neat homopolymers and their blends with and without blowing agent are measured with a high-pressure slit die rheometer. Differential scanning calorimetry (DSC) is performed in a Seiko-Haake DSC
30 calorimeter from Haake of Paramus, New Jersey at a heating rate of 10°C/min under a nitrogen purge.

Example 61

A sample of poly(vinylidene fluoride) is premixed to a desired concentration with poly(methyl methacrylate) and placed into the hopper of a single-screw extruder. The polymer mixture is then extruded at a temperature of 200°C. During the course of the extrusion carbon dioxide is injected at 25°C, 4500 psi such that the polymer/carbon dioxide mixture forms a homogeneous phase having 5 percent by weight of carbon dioxide. The extruded mixture is cooled to 150°C, and exits via a nozzle producing a microcellular foam.

Example 62

The procedure according to Example 61 is carried out except that syndiotactic polystyrene is premixed to a desired concentration with poly(methyl methacrylate) and then foamed.

Example 63

The procedure according to Example 61 is carried out except that poly(vinyl chloride) is premixed to a desired concentration with poly(ethyl acrylate) and then foamed.

Example 64

The procedure according to Example 61 is carried out except that poly(ethylene oxide) is premixed to a desired concentration with poly(methyl methacrylate) and then foamed.

Example 65

The procedure according to Example 61 is carried out except that poly(ethylene terephthalate) is premixed to a desired concentration with poly(ethylene naphthalate) and then foamed.

Example 66

The procedure according to Example 61 is carried out except that poly(vinyl chloride) is premixed to a desired concentration with poly(ε-caprolactone) and then foamed.

5

Example 67

The procedure according to Example 61 is carried out except that polyethylene is premixed to a desired concentration with polypropylene and then foamed.

10

Example 68

The procedure according to Example 61 is carried out except that poly(ether imide) is premixed to a desired concentration with poly(ethylene terephthalate) and then foamed.

15

Example 69

The procedure according to Example 61 is carried out except that syndiotactic polystyrene is premixed to a desired concentration with poly(phenylene oxide) and then foamed.

20

Example 70

The procedure according to Example 61 is carried out except that poly(vinylidene fluoride) is premixed to a desired concentration with poly(1,4-butylene adipate) and then foamed.

25

The invention is illustrated by reference to the above embodiments. It should be appreciated however that the invention is not limited to these embodiments but is instead defined by the claims that follow.